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Computed Activation Energies for Reactions of O_2, N_2, NO, N_2O, NO_2, CO, and CO_2

DECEMBER 1967

Prepared by S. W. MAYER
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AIR FORCE SYSTEMS COMMAND
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FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04695-67-C-0158 and documents research carried out from March 1967 through October 1967. It was submitted for review and approval on 5 January 1968 to Captain Keith S. Peyton, SMTAP.

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Approved

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R. A. Hartunian, Director
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Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Keith S. Peyton

Keith S. Peyton, Captain, USAF
Project Officer

ABSTRACT

A method is described for calculating the activation energies of bimolecular reactions of such multivalent gaseous compounds as O_2, N_2, NO, N_2O, NO_2, CO, and CO_2. It is also applicable to the monatomic reactants O, N, and H and to the OH radical. The method uses relationships between dissociation energy, bond length, vibrational wavenumber, and bond order. It avoids the use of adjustable parameters. The agreement between calculated and experimental activation energies is very good when spin conservation in the transition state is considered in the computation procedure. A convenient rule has also been formulated that predicts the activation energy will be negligible in bimolecular reactions between radicals when the transition-state formula corresponds to that of a compound having stable bonds. No exceptions to this rule have been found. The method is applicable to computing rates needed for nonequilibrium calculations of propellant performance and of reentry behavior.

CONTENTS

TABLES

I. INTRODUCTION

The reaction rates of compounds containing oxygen, nitrogen, or carbon are important in determining the nonequilibrium effects on propellant performance of the fuels and oxidizers composed of these elements. In reentry through the earth's atmosphere, particularly if ablation of carbonaceous materials is involved, the rates of reactions of such compounds must affect reentry nonequilibrium phenomena. These rates can also be of considerable significance in affecting propellant ignition, jet flames, supersonic wind tunnels and upper-astmosphere composition. They can also influence areas of peripheral aerospace interest such as air pollution and the internal combustion engine.

Although the activation energies and rate constants for some of the reactions of these compounds have been measured, a basis for predicting and understanding their kinetic behavior has not been established. For example, the activation energies of the exothermic reactions $NO_2 + O = NO + O_2$ and $NO_2 + H = NO + OH$ are zero, but the activation energies of the two exothermic reactions $N_2O + NO = N_2 + NO_2$ and $O_2 + CO = O + CO_2$ are each 50 kcal/mole. This difference of 50 kcal/mole in activation energy provides the huge factor of more than 10^{35} toward reducing the rate constant of the latter two reactions. Since the preexponential factor of the Arrhenius rate constant equation is closely related physically to the readily calculated collision frequency, the preexponential factor can usually be predicted within a factor of less than 5 for similar reactions. Consequently, the most important problem in the prediction of rate constants for these multivalent reactions is that of computing the activation energies. The computational method developed in this study provides an explanation for these highly significant differences in activation energies. The method is also to be applied in the computation of rate constants of the important O, N, and C compounds in those reactions for which no experimental kinetic data exist.

Transition-state computations[1,2] of activation energies and rate constants for hydrogen-atom transfers in the gas phase exhibit good agreement with measured activation energies and rate constants when several trial assumptions involving bond energy, bond order, and bond length interrelationships are used. Included are the assumptions: (1) that the Pauling[3] "rule" for the relationship between bond length and bond order applies in the transition state; (2) that the Lennard-Jones 6-12 energy and distance parameters[4] for the noble gases represent the zero bond order energies and internuclear distances for elements in the corresponding rows of the periodic tables; (3) that an approximately linear relationship exists between the logarithm of bond energy and the logarithm of bond order[1]; (4) that the triplet repulsion energy arising from uncoupled spins in the transition state is represented by a Sato[5] anti-Morse function similar to that for triplet ${}^3\Sigma_u^+$ state of H_2. Instead of having to use these assumptions for computing kinetic parameters, a quantitative quantum-mechanical treatment would clearly be preferable, but a tractable quantum treatment does not exist for complex multielectron reacting systems. It is, nevertheless, possible (although open to serious question) that the changes in potential energy of dissociating bonds or forming bonds may be described, as a function of bond length or nominal bond order, within some arbitrary error such as 2 kcal per bond by postulates derived empirically from energy data for a series of bonds covering a range of bond orders.[3]

The aforementioned activation energy computing method does not utilize adjustable parameters. It does, however, use a tentative model of the transfer reaction

$$AH + B = \underset{n_1}{A\cdots}\ H\cdots\underset{n_2}{B} = A + HB \qquad (1)$$

whereby the sum of the bond orders n_1 and n_2 in the transition state is constant at unity, corresponding to the initial univalent bond order of the reactant AH and of the final bond order of the product HB. For this model, the

activation energy of the transition state is calculated for one line,[1,2] rather than a surface as in the London-Eyring-Polanyi method[6] of attempting to compute activation energy.

Because of the relative success[1,2] of this bond-energy bond-order (BEBO) model in predicting rate constants for H-atom transfers, it was decided to investigate its applicability to reactions in which the transferred univalent atom was larger than the hydrogen atom and, eventually, to reactions in which multivalent atoms were transferred. Thus, propellant and reentry reactions involving compounds of O, N, F, Cl, C, etc., could be covered. A reduced-variable treatment was introduced[7] so that larger, univalent atoms such as the halogens were scaled relative to hydrogen. The computed activation energies and rate constants were found to agree very well with the measured values of those relatively few halogen transfer reactions for which the experimental kinetic data were available.[7] The number of such reactions was too few to produce much confidence in the modified BEBO method when not limited to H-atom transfers, particularly since the measured activation energies were all quite low (3 kcal/mole or less).

There is, however, a relatively large quantity of kinetic data available for atom transfer reactions involving oxygen or nitrogen atoms, and the measured activation energy barriers for these transfers include rather high values as well as low values. Modifications of the method[1] were needed because of the multivalent character of the dissociating bonds or forming bonds involving nitrogen or oxygen in the transition state. The multivalency clearly voided the use of the simple BEBO reaction model in which it was postulated that n_2 equals 1 - n for univalent bonds in the transition state. This assumption is equivalent to stating that the bond order n_2 of H$\cdots$B is equal to the decrease in bond order n_1 of the dissociating bond A$\cdots$H from its initial bond order. An extension of this trial assumption to multivalent transfers can be made by choosing a transition-state model in which the bond order n_2 continues to be linearly related to the decrease in the bond order of the dissociating bond A$\cdots$X, where X is the transferred atom. The computation procedure associated with this model is described in the next section. Comparison of experimentally determined

activation energies with those computed from this model with spin conservation applied to the transition state showed very good agreement, when it is considered that the formula of the transition state in some cases corresponded with the formula of a stable compound (e.g., N_2O). Activation energies were computed for other bond dissociation-bond formation models such as those corresponding to nonconservation of spin, or bond energies rather than dissociation energies. The computation procedures for these other, relatively unsatisfactory models are described in the latter portions of the next section.

II. COMPUTATION PROCEDURES

A. MULTIVALENT, DISSOCIATION ENERGY

The aforementioned transition-state model for multivalent transfers in which the bond order n_2 of the formed bond X···B was linearly dependent on the decrease in bond order of the dissociating bond was satisfied by the relationship

$$n_2 = (n_{XB}/n_{AX})\,(n_{AX}-n_1) \tag{2}$$

where n_{AX} and n_{XB} are, respectively, the initial bond order of the reactant AX and the final bond order of the product XB, X is the transferred atom (e.g., nitrogen or oxygen), and n_1 is the bond order of A···X in the transition state. Equation (2) meets the requirement that when n_2 is zero (at the initiation of the reaction) n_1 equals n_{AX}, and that n_2 equals n_{XB} when n_1 is zero at the conclusion of the bimolecular transfer reaction. When X is a univalent atom such as hydrogen, Eq. (2) reduces to the BEBO trial assumption that $n_1 + n_2$ equals 1.

In order to compute activation energies for transfers involving a multivalent bond by a modified BEBO method, it was necessary to extend the bond-energy bond-order relationship to orders above 1. Since a linear relationship between log D_e (where D_e is the gas-phase dissociation potential energy of the bond) and log n was used for bond order not exceeding 1, a relatively simple modification of the BEBO method was made by also using a linear log D_e/log n relationship between n_{AX} (or n_{XB}) and n equal to 1. Then, the slope π_{AX} of the line for the multivalent region is given by

$$\pi_{AX} = [\log (D_e/D_1)]/\log n_{AX} \tag{3}$$

where D_1 is the dissociation potential energy of the bond A-X of bond order 1. D_e includes the zero-point energy, as shown in Table I, since it is based on the minimum of the potential energy curve.[8] For diatomic species, the dissociation energy is equal to the bond energy B_e, but, as shown in Table I,

TABLE I. Molecular and Bond Data[a]

Data	Molecules							
	N_2	NO	O_2	CO	NO_2	N_2O	N(NO)	CO_2
Dissociation energy, D_e, kcal/mole	228.6	152.8	120.3	258.9	73.7	41.0	116.2	128.4
Bond length, r_e, 10^{-8} cm	1.098	1.151	1.207	1.128	1.197	1.186	1.126	1.159
Vibrational wavenumber, ω_e, cm^{-1}	2358	1904	1580	2170	1330	1410	1685	1720
Bond energy, B_e, kcal/mole	228.6	152.8	120.3	258.9	113.2	110	158	193.5
Bond order	3.0	2.5	2.0	3.0	1.75	1.75	2.5	2.0
Ground state	$^1\Sigma$	$^2\pi$	$^3\Sigma$	$^1\Sigma$	$^2\Sigma$	$^1\Sigma$	$^1\Sigma$	$^1\Sigma$
Single-bond values used								
Dissociation energy, D_1, kcal/mole	39.7	49.5	35.0	85.7	32.2	18.1	29.1	55.6
Bond length, r_1, 10^{-8} cm	1.48	1.44	1.47	1.43	1.44	1.44	1.48	1.43
Vibrational wavenumber, ω_1, cm^{-1}	1370	1220	1120	1180	1080	1090	1105	1180
Bond energy, B_1, kcal/mole	39.7	49.5	35.0	85.7	49.5	49.5	39.7	84.0

[a] The JANAF Thermochemical Tables (with supplements to December 1966) were the primary source of data. Energies were computed on the basis of the potential energy curve and, consequently, included the zero-point energy. In polyatomic molecules, D_e for the bond broken or formed is not equal to the bond energy since the other bonds in the molecule change in energy when one bond is broken or formed. For N_2O, which can dissociate to form either N_2 or NO, the total gas-phase dissociation energy of 268 was partitioned between the ON and NN bonds on the basis of their estimated bond orders.

this equality does not hold for polyatomic species since the bond energies of the other bonds in the molecule generally change when a bond is broken or formed.[3] The values of D_e in Table I were obtained in a straightforward manner from thermochemical data,[8] but the values of D_1 for the triatomic molecules were estimated because they have not been measured. The estimations were based on the simple assumption that the relationship of D_1 to B_1 was in the same proportion as D_e to B_e

$$D_1/B_1 = D_e/B_e \tag{4}$$

This expression also implies that the slope π_{AX} is unchanged if B_e/B_1 is used in Eq. (3) instead of D_e/D_1.

With these modifications, the potential energy V of transition-state formation in multivalent bimolecular transfer reactions was calculated in a manner similar to that used for univalent transfers.[1,2]

$$V = (D_{e,AX} - D_{1,AX} n_1^{\pi_{AX}}) - D_{1,XB} n_2^{\pi_{XB}} + V_r \tag{5}$$

where V_r is the triplet repulsion as calculated by the reduced variable treatment of Eq. (10) in Ref. 7. When a bond order, n_1 or n_2, is less than 1, the slope π in Eq. (5) is replaced by the slope p calculated for the bond-order region below 1. In a manner similar to that of previous investigations,[1,2] the computer program modified for multivalent bonds determines the value of n_2 that corresponds to the peak in the potential energy V of the linear transition-state model A···X···B. The computed activation energy for this model is equal to the potential energy peak height plus a small zero-point energy correction.[6]

B. SPIN CONSERVATION IN THE TRANSITION STATE

The dissociation energies D_e shown in Table I correspond, as is customary, to dissociation to ground-state products. In thermal dissociation, the ground-state atomic oxygen dissociated from $CO_2(^1\Sigma)$ and $N_2O(^1\Sigma)$ would

be triplet $O(^3P)$, but spin would be conserved if a singlet $O(^1D)$ atom were dissociated from the parent molecule. For these bimolecular transfers, it is not known whether dissociation of CO_2 or N_2O starts by splitting off a singlet $O(^1D)$ atom and is followed by spin conversion deexcitation of the singlet to the triplet $O(^3P)$. It is conceivable that prior to the dissociation the molecule transforms to an excited state via an internal spin change and that $O(^3P)$ is then formed directly by dissociating from an excited molecule, or the oxygen atom dissociated from ground state N_2O or CO_2 could cross over to $O(^3P)$. From a kinetics point of view, it appears that the most direct mode of beginning to break the oxygen bond in bimolecular transfers involving N_2O or CO_2 could well be by the formation of singlet $O(^1D)$. From that point of view, it is clearly desirable to consider a transition-state model, when N_2O or CO_2 are involved in the bimolecular transfer of an oxygen atom, in which the dissociating oxygen (i.e., X in A···X···B) is in the $O(^1D)$ state. This can be done quite readily in computations of the activation energy by adding the difference in energy between $O(^3P)$ and $O(^1D)$ (45.4 kcal/mole) to D_e when the described computation procedure is used for multivalent transfers. In contrast with the dissociation spin-conservation requirements for N_2O and CO_2, it is possible for ground state $O(^3P)$ to dissociate directly with spin conservation from the other molecules of Table I: NO, CO, NO_2, and O_2. Consequently, a transition-state model for oxygen transfers involving only the latter molecules need not consider the possibility that $O(^1D)$ is the state of the transferred atom.

C. BOND FORMATION IN THE TRANSITION STATE WITHOUT CORRESPONDING DISSOCIATION

When the modified BEBO method was applied[1, 2, 7] to univalent bonds such as those in F_2 or H_2, the model of the transition state logically involved the assumption that dissociation of the bond of reactant AX must occur in proportion to the formation of the product bond XB. This proportionality is expected since the XB bond is formed with the participation of an electron

that had been used in the AX bond. In multivalent reactions, the situation can be more complex. For example, in the case of NO_2 reactant, the valence electrons are not in a completely bonded form, as indicated by the electron spin. It is possible, therefore, that a model for the oxygen-transfer reaction of NO_2 with H could consist of the formation of a species such as H···ONO, where the bond order of H···O increases without a similar decrease in the ON bond. In this study, the criterion for selecting those transition states for which this model was considered possibly applicable was the existence of a stable compound that corresponded to the transition-state formula. In the cited case, nitrous acid would be the stable compound, with a dissociation potential energy of 78 kcal/mole for the HO bond.[8] Other compounds with formulas similar to those of relevant transition-state models are N_2O, NO_2, and O_3. Computations of activation energy based on this model can be made by subtracting a term from the right-hand member of Eq. (5) that corresponds to the potential energy of the bond formed by one reactant with the other reactant (e.g., H and ONO).

D. BOND-ENERGY DISSOCIATION

The dissociation models previously used[1] for polyatomic molecules allow the dissociation of an atom from a reactant to proceed slowly enough so that the other bonds in the reactant reach their ground state before the A···X bond (where A is not monatomic) is completely broken. Consequently, the dissociation energy rather than the bond energy was used for computations based on this model. It is conceivable, however, that for some polyatomic molecules the bond A···X may break so rapidly in the transition state that the other bonds in A remain unchanged in the transition state. When computations were made for oxygen or nitrogen transfers based on this model, the calculated activation energies did not usually agree well with the measured values. For this model, computations were made by using the bond energy data of Table I rather than the dissociation energies.

E. SIMULTANEOUS POLYVALENT BOND FORMATION AND DISSOCIATION

It is characteristic of the transition-state models previously described that bond formation proceeds first via formation of the single bond, which then becomes a polyvalent bond as the reaction progresses. It is clearly possible that the formation of a polyvalent bond in the transition state does not proceed through any recognizable single-bond state such as those for which data are presented in Table I, but that the molecular orbital changes involved in the formation of a polyvalent bond proceed directly from the zero bond to the final bond without the intermediate step of passing through a bond characteristic of single bonds in stable molecules. Similarly, the dissociation of the polyvalent bond A··X in the transition state could proceed directly to the zero-bond state without following the potential-energy bond-order path suggested by the dissociation energy D_1 of a single bond. By using the D_e and r_e of Table I and the Johnston-Parr trial assumption[1] that the Lennard-Jones 6-12 energy and distance parameters for neon[4] represent the zero bond-order energies and internuclear distances of N and O bonds, values of π_{AX} and π_{XB} were calculated for use in Eq. (5) over the entire bond-order range rather than limiting the use of π_{AX} and π_{XB} to bond orders above 1. The activation energies computed for this model gave poor agreement with experiment for most of the reactions studied, but not for reactions of an atom with a diatomic species. In the latter cases, the transition state is triatomic, and the only bonds in the transition state are the breaking and forming bonds.

III. RESULTS AND DISCUSSION

Computed activation energies are compared in Table II with experimental activation energies; none of the reactions in Table II are of the atomic plus diatomic type. The computed E_0's of particular interest are in the spin conservation column. This column summarizes the computed E_0's obtained by combining the postulate of spin conservation for dissociation of the multivalent bond, described in the section on Computation Procedures, with the linear bond-order relationships for multivalent bonds as embodied in Eqs. (2) through (5). The agreement between the E_0's computed by this method and the experimental E_0's is usually quite good. Among this first group of reactions, spin conservation involves the formation or reaction of an $O(^1D)$ atom if CO_2 or N_2O is a reactant or product, and the agreement between computed and measured E_0's is much superior when spin conservation is assumed. The multivalent dissociation energy column summarizes the E_0's computed with the spin conservation ignored. The latter dissociation model provides satisfactory agreement only for those reactions in which the dissociation and formation of the bonds can be accomplished via ground-state species as in the $NO + NO = N + NO_2$ reaction.

The no triplet column presents E_0's computed by the procedure used for the spin conservation column, except that triplet repulsion V_r was arbitrarily set at 0. From the results listed in this column it can be seen that, for almost all of these reactions, the triplet repulsion made only a small contribution to the activation energy, relative to the contributions of the bonding terms in Eq. (5). The single-bond energy column lists E_0's computed by the procedures used for the spin conservation column, except that the single-bond energy B_1 was used for Eqs. (3) and (5), rather than the corresponding dissociation energy D_1. It is evidently incorrect, as anticipated, to use B_1 rather than D_1 since the computed E_0's do not generally exhibit satisfactory agreement with experiment when B_1 is thus employed.

TABLE II. Comparison of Computed Activation Energies With Observed Activation Energies.

Reaction AX+B = A+BX	Observed E_0	Computed Activation Energies[a]					
		Spin conservation	Multi. dissoc. energy	No triplet	Single-bond energy	Mult.-bond energy	Poly. simultaneous
$N_2O+NO = N_2+NO_2$	50[b,c]	48	2	46	31	13	1
$N_2O+O = N_2+O_2$	27[d]	29	0	26	0	35	-
$N_2O+H_2 = N_2+OH$	15[e]	15	0	14	0	1	0
$O_2+CO = O+CO_2$	50[f]	49	37	48	-	73	5
$HO+CO = H+CO_2$	0[g]	1	0	0	0	-	-
$NO_2+CO = NO+CO_2$	32[h]	28	2	26	0	34	0
$ONN+O = ON+NO$	27[i,j]	29	24	25	48	40	0
$NO_2+N = ON+NO$	0[d]	-	0	0	0	1	0

[a] Energies expressed in kcal/mole.

[b] F. Kaufman and J. R. Kelso, J. Chem. Phys. 23, 602 (1955).

[c] E. S. Fishburne and R. Edse, J. Chem. Phys. 41, 1297 (1964).

[d] D. Gutman, R. L. Belford, A. J. Hay, and R. Panirov, J. Phys. Chem. 70, 1793 (1966).

[e] G. Dixon-Lewis, M. M. Sutton, and A. Williams, Tenth International Symposium on Combustion, Combustion Institute, Pittsburgh, Pa. (1965), p. 495.

[f] K. G. P. Sulzmann, B. F. Myers, and E. R. Bartle, J. Chem. Phys. 42, 3969 (1965).

[g] G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, J. Chem. Phys. 44, 2877 (1966).

[h] H. S. Johnston, W. A. Bonner, and D. J. Wilson, J. Chem. Phys. 26, 1002 (1957).

[i] K. Schofield, Planet. Space Sci. 15, 643 (1967).

[j] R. M. Fristrom and A. A. Westenberg, Flame Structure, McGraw-Hill Book Co., Inc. New York, (1965), p. 355, 371, 372.

For the multivalent bond-energy column, the method described in the Computation Procedures section under "Bond-Energy Dissociation" was used. Examination of the computed E_0's in this column of Table II shows that they do not generally agree with the experimental E_0's,although there are some cases of agreement. For the polyvalent simultaneous column, the method used was described in the Computation Procedures section under "Simultaneous Polyvalent Bond Formation and Dissociation." For those reactions having a transition state with more than two bonds, this model for the bonding changes during a reaction and does not give agreement with experiment.

The first six reactions of Table III are the only ones in the tables for which the structural formula of the transition state is similar to that of a stable species[8] (e.g., HONO, N_2O, NO_2, NO_3, O_3, and HO_2). A stable species can be defined, in this context, as one in which no bond dissociation energy is less than 25 kcal/mole. For this specific class of reactions, E_0 can be computed as outlined under "Bond Formation in the Transition State without Corresponding Dissociation" of the Computation Procedures section. For this group of reactions between two radicals, E_0 in the exothermic direction is almost zero, apparently because sufficient energy is initially provided by the preliminary partial formation of the new bond in the transition state to supply the subsequent dissociation energy requirement of the old bond with virtually no potential energy of activation. It is expected that the absence of activation energy barriers will be generally characteristic of bimolecular transfer reactions for which the transition-state structural formula corresponds to that of a stable compound, if the bond formed between the two radical reactants has a binding energy larger than the activation energy predicted by the appropriate model of Table III. Of the six reactions in this group in Table III, four are the monatomic-plus-diatomic polyvalent reaction type for which the simultaneous bond-formation model may be justified. The potential value of the simultaneous model is further indicated by the results in Table III for the last reaction, $NO + O = N + O_2$, which does

TABLE III. Reactions That Have a Transition-State Formula Similar to a Stable-Molecule Formula

Reaction AX+B = A+BX	Transition-state formula	Observed E_0	Computed E_0[a]		Energy[b] of new bond (kcal/mole)
			Multi. dissoc. energy	Poly. simultaneous	
ONO+H = ON+OH	HNO_2	0[c]	1	-	78
ONO+O = ON+O_2	NO_3	0[d]	3	-	49
ON+N = O+N_2	N_2O	0[d]	25	0	61
ON+O = O+NO	NO_2	~0[e]	25	1	72
O_2+O = O+O_2	O_3	~0[e]	51	4	26
HO+O = H+O_2	HO_2	0[f]	25	5	63
O_2+N = O+NO	--	0[f]	27	8	--

[a] In all these reactions, spin conservation in the transition state can occur without involving excited atoms, such as $O(^1D)$ or $N(^2D)$. Therefore, the E_0 computed by the multivalent dissociation-energy model is equal in these cases to the E_0 computed for the spin-conservation model.

[b] Bond-energy data based on JANAF tables. In each of these six reactions, this bond energy is easily sufficient to supply all the activation energy that would have been needed, based on E_0 computed by the appropriate model. Consequently, observed E_0 should be negligible (i.e., 0 or 1 kcal/mole).

[c] L. F. Phillips and H. I. Schiff, J. Chem. Phys. 37 1233 (1962).

[d] L. F. Phillips and H. I. Schiff, J. Chem. Phys. 36, 1509 (1962).

[e] J. T. Herron and F. S. Klein, J. Chem. Phys. 40, 2731 (1964).
F. S. Klein and J. T. Herron, J. Chem. Phys. 41, 1285 (1964).

[f] R. M. Fristrom and A. A. Westenberg, Flame Structure, McGraw-Hill Book Co., Inc., New York (1965), p. 355, 371, 372.

not have a transition-state formula that corresponds to a stable compound.[8] The E_0 computed by the simultaneous model for this reaction agrees very well with experiment, whereas the E_0's computed by models involving typical single-bond energies for N-O and O-O are much too high.

The agreement between computed and experimental E_0's, particularly for spin-conservation dissociation in the transition state, suggests that it may now be possible to understand important and previously unrecognized characteristics of bimolecular chemical reactions to an extent that was not hitherto possible. To summarize, the trial postulates found to be of value in these computations are: (1) spin conservation for the transferred atom is maintained in the transition state; (2) the activation energy (exothermic direction) is generally almost zero when the structural formula of the transition state corresponds to that of a reasonably stable molecule; (3) the dependence of potential energy on bond order in the transition state is represented within about 2 kcal/mole by Eq. (5), as supplemented by Eqs. (2) through (4); and (4) in reactions of atoms with diatomics involving polyvalent bonds, the direct, simultaneous formation and dissociation of polyvalent bonds occur. These trial postulates provide a hitherto nonexistent basis for calculating activation energies and estimating rate constants of multivalent transfer reactions when no experimental rate data are available.

REFERENCES

1. H. S. Johnston and C. Parr, J. Am. Chem. Soc. 85, 2544 (1963).
2. S. W. Mayer, L. Schieler, and H. S. Johnston, J. Chem. Phys. 45, 385 (1966).
3. L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, N. Y. (1960).
4. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, Inc., N. Y. (1964).
5. S. Sato, J. Chem. Phys. 23, 592, 2465 (1955).
6. S. Glasstone, K. J. Laidler, and H. Eyring, Theory of Rate Processes, McGraw-Hill Book Co., Inc., N. Y. (1941).
7. S. W. Mayer, L. Schieler, and H. S. Johnston, Proceedings of the Eleventh International Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa. (1967) p. 837.
8. D. R. Stull, ed., JANAF Thermochemical Tables, with Supplements, Dow Chemical Co., Midland, Mich. (1966).

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13. ABSTRACT

A method is described for calculating the activation energies of bimolecular reactions of such multivalent gaseous compounds as O_2, N_2, NO, N_2O, NO_2, CO, and CO_2. It is also applicable to the monatomic reactants O, N, and H and to the OH radical. The method uses relationships between dissociation energy, bond length, vibrational wavenumber, and bond order. It avoids the use of adjustable parameters. The agreement between calculated and experimental activation energies is very good when spin conservation in the transition state is considered in the computation procedure. A convenient rule has also been formulated that predicts the activation energy will be negligible in bimolecular reactions between radicals when the transition-state formula corresponds to that of a compound having stable bonds. No exceptions to this rule have been found. The method is applicable to computing rates needed for nonequilibrium calculations of propellant performance and of reentry behavior.

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Unsymmetrical Dimethylhydrazine

Abstract (Continued)